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N⁺ ion implantation of Ti6Al4V alloy and UHMWPE for total joint replacement application

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ABSTRACT: Multidirectional pin-on-plate tribological wear tests were performed to evaluate and compare the tribological behavior of N⁺ ion-implanted and unmodified Ti6Al4V/ultra high molecular weight polyethylene (UHMWPE) sliding couples, for total joint replacement (TJR) applications. Knoop microhardness indentations were measured and an increase in surface hardness of more than twofold and up to four times, respectively, was observed for the Ti6Al4V alloy and UHMWPE after N⁺ ion implantation, at a load of 1 gf. Increase in hardness was attributed to the formation of TiN precipitates and cross-linking in the alloy and polymer, respectively. Wear test results showed that N⁺ ion implantation reduced surface wear of the Ti6Al4V alloy and, in turn, significantly reduced the wear of the mating UHMWPE.

Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), non-contacting interferometry and optical microscopy were used to characterize both modified and unmodified material surfaces prior to and after tribological wear tests. The results indicated that N⁺ ion-implanted Ti6Al4V/UHMWPE sliding couples were distinctly superior to the unmodified sliding couples, and demonstrated a definite potential for the use of N⁺ ion-implanted Ti6Al4V and implanted UHMWPE as load bearing surfaces in TJR prostheses. (*Journal of Applied Biomaterials & Biomechanics* 2003; 1: 164-71)

KEY WORDS: Total joint replacements, Ion implantation, Wear, Hardness, Ti6Al4V alloy, UHMWPE

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INTRODUCTION

Ti6Al4V alloys are among the most biocompatible biomaterials and have in recent years gained increased usage in total joint replacements (TJR) because of their combination of excellent fatigue strength, good corrosion resistance, low density and elastic modulus, excellent formability and machinability (1-4). They have a low rigidity compared with other metallic biomaterials used for TJRs, for example, stainless steel and cobalt chrome alloys; and therefore, have the theoretical advantage of reducing the incidence of proximal bone resorption due to stress shielding (4, 5). The reaction of tissue adjacent to the Ti6Al4V alloy in joint replacements is extremely benign, and direct bone ingrowth or osseointegration with its implants does occur (4).

However, despite the many favorable characteristics of the alloy, it has relatively poor surface wear resistance. A series of clinical retrieval and experimental wear studies (5-10) showed that when sliding surfaces of the femoral components of artificial joints are made from Ti6Al4V, wear can lead to black staining of the surrounding tissue and failure of the joints, and that Ti6Al4V with no surface treatment is not suitable for *in vivo* bearing applications due to the poor surface wear resistance. As load bearing components of joint prostheses, they normally articulate against an ultra high molecular weight polyethylene (UHMWPE) counter bearing surface, and this combination has shown a relatively poor tribological performance with the production of particulate debris from both surfaces under clinical and laboratory conditions (11). UHMWPE use as the bearing surface in TJRs is often limited

by low hardness, poor wear resistance and wettability considerations and it is widely documented that the main trigger mechanism for macrophagic osteolysis and loosening is the release of sub-micron UHMWPE wear particles (4, 12, 13).

N^+ ion implantation has been successful in biomaterial surface modifications, such as in improving the wear resistance of artificial joint components (1-3). It offers a number of advantages over other modification techniques such as surface coatings, because it facilitates both chemical and structural modification of the near surface volume of a material, without the creation of a discrete interface between modified and unmodified volume. In so doing, a gradual transition in chemistry, structure and properties is produced, reducing the possibility of interfacial delamination. N^+ ion implantation has proved a potential method for improving the surface wear of Ti6Al4V alloy (14, 15).

In this study, N^+ ions were implanted into Ti6Al4V alloy and UHMWPE, to enhance the tribological characteristics of the alloy surface and minimize wear of the mating UHMWPE, on a multidirectional pin-on-plate machine under simulated *in vivo* tribological conditions.

MATERIALS AND METHODS

Commercially available Ti6Al4V and UHMWPE materials (Depuy Johnson & Johnson, Leeds, UK), were investigated in this study. The alloy was supplied hot drawn and displayed a duplex $\alpha + \beta$ microstructure (Fig. 1). Tribological plate specimens were prepared by a heat cut-off saw (Beuhler Iso Cut) followed by conventional wet SiC grinding and diamond paste (6 μm and 1 μm polishing). Samples were polished to a better than 0.01 μm , arithmetic mean surface roughness (R_a). An optical non-contacting interferometry was used to characterize the R_a . UHMWPE wear pins with a 5 mm diameter wear face and 18 mm in length were machined from the bulk material, and microtomed to remove the machining marks. The metallic plates were degreased with acetone and polymeric wear pins ultrasonically cleaned to remove any loose particles prior to ion implantation. N^+ ion implantation was performed at Tech-Ni-Plant, Birmingham, using the Zymet Z-100, 100 KeV, 10 mA ion implantation system. The Ti6Al4V plates were implanted with ion doses of $2 \times 10^{17} N^+$ ions/cm² at an accelerating voltage of 90 KeV, and the UHMWPE wear pins with $5 \times 10^{15} N^+$ ions/cm² at an accelerating voltage of 80 KeV. A lower dose and energy were selected for the polymer material, due to the ease of

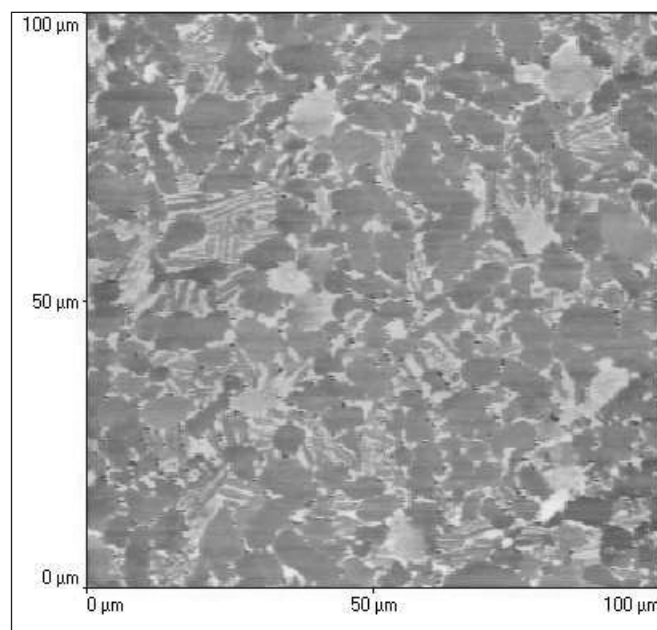


Fig. 1 - AFM image of the etched Ti6Al4V alloy showing the classic two-phase $\alpha + \beta$ microstructure.

thermal damage. The target temperature was kept <100 °C and the residual gas pressure in the implantation chamber <1 x 10⁻⁵ Pa.

Microhardness was measured by evaluating the penetration depth with an applied load. A Knoop microhardness indenter was used, being more appropriate for evaluating the mechanical property at the extremely thin surface layer, rather than the Vickers indenter, which measures bulk hardness. The indentations were normal to the surface and carried out with a load range of 1-25 gf. Ten measurements were recorded at each load, and the average hardness at the different loads calculated. Deviations from the average values at the different loads were less than 15%.

Modified and unmodified surfaces were evaluated prior to and after wear tests, mainly using atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), non-contacting interferometry and optical microscopy. A TopoMetrix TMX 1010 AFM was used with two primary scanning modes, contact and non-contact, referring to whether or not the scanning probe actually comes into physical contact with the sample surface. It comprised of a force-sensing probe, piezoelectric ceramics for positioning the probe, an electronic control unit, and a computer for controlling the scan parameters and generating and presenting images (16). It is a simple method involving the least instrument variables for gathering topographic information even to the atomic level resolution.

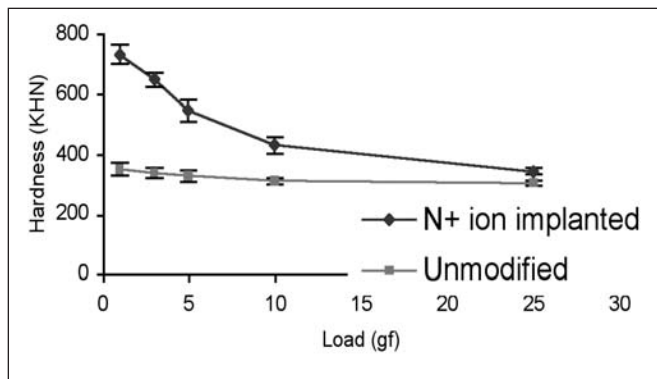


Fig. 2 - Knoop surface microhardness of the Ti6Al4V alloy.

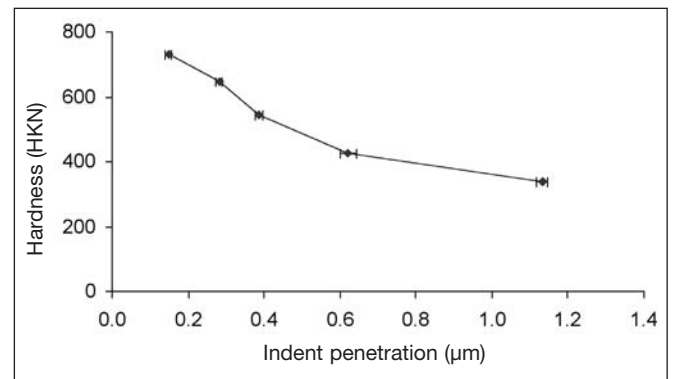


Fig. 3 - Depth dependence of Knoop microhardness for ion implanted Ti6Al4V.

To compare simply the wear characteristics of the N⁺ ion-implanted and non-implanted material couples, pin-on-plate wear tests were chosen. They are widely used as screening devices in wear studies (17-19) due to their more realistic motion compared with *in vivo* conditions. The device used in this study employed both reciprocation and rotation motion, which produces a crossing of the wear paths, and is also able to offer a better simulation of the conditions encountered in the load bearing joints of the lower limb than the reciprocation alone geometry pin-on-plate wear machine (17, 18). The conditions for the wear tests were as follows: a 40 N test load applied along the longitudinal axis of the UHMWPE wear pin such that the average contact stress was 2.04 MPa; a reciprocation and rotation speed of 1 Hz, 30% bovine serum lubrication with sodium azide as a preservative; and sliding distance of 36 mm/cycle. Each test used four UHMWPE pins and Ti6Al4V plates, and wear was monitored at regular intervals by a gravimetric technique using a balance sensitive to 2 μg. An unloaded soak control pin enabled compensation for fluid absorption. The cleaning protocol in the ASTM standard F732-82/F732-00 was followed (20, 21). UHMWPE volume loss (V) was plotted against the sliding distance (S) and the wear factor (k_o) calculated from the slope of the graph divided by the normal load (L). The wear factor is given by:

$$k_o = V/LS \text{ (mm}^3/\text{Nm)}$$

RESULTS AND DISCUSSION

The hardness of the modified materials, increased with a decreasing indentation load, and the highest values were recorded at an indentation load of 1 gf. The recorded mean hardness values were plotted

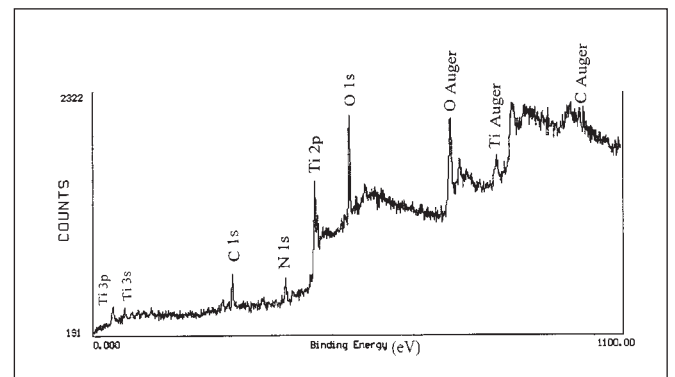


Fig. 4 - XPS energy spectrum of ion implanted Ti6Al4V.

TABLE I - MEAN KNOOP SURFACE HARDNESS VALUES

Mean hardness at a load of 1 gf (HKN)			
Ti6Al4V	N ⁺ ion-implanted Ti6Al4V	UHMWPE	N ⁺ ion-implanted UHMWPE
347 ± 20	730 ± 32	3.4 ± 0.5	12.8 ± 1.6

against load (Fig. 2) and indent penetration depth (Fig. 3), for the Ti6Al4V alloy. Knoop indent penetration depth at each load was calculated from the Knoop geometry, using trigonometry during the microhardness measurements. Table I shows the mean hardness values measured for modified and unmodified Ti6Al4V plates, and UHMWPE wear pins at a load of 1 gf.

The depth of N⁺ ion implantation varied from 0.1 to <1 μm depending on the implantation energy, and was typically within 0.2-0.5 μm in metals (1, 22, 23). Figure 3 clearly shows the surface dependence of the ion implantation modification and the lack of

discrete interface between modified and unmodified material. Clearly, at a load of between 1 and 5 gf, the indentation depth on modified Ti6Al4V was within the depth of implantation reported; therefore, the increase in hardness was mainly due to the effect of N⁺ ion implantation modification.

N⁺ ion implantation into Ti6Al4V alloys causes changes in the chemical structure of the surface by the creation of hard phase nitride precipitates producing a hardening effect, mainly due to precipitation strengthening mechanisms (11, 24-26). Figure 4 shows the XPS chemical surface analysis survey spectrum of the implanted Ti6Al4V, where the binding energy position of N 1s was clearly discernable, and an indication of N presence on the surface material, which was not present on the surface of the unmodified material. High-resolution XPS collections of the Ti 2p and N 1s were made, and the Ti 2p peak was observed to exhibit a twin doublet comprising TiO₂ and minor TiN. The N 1s region showed a triple peak structure, the main one being TiN at 392.2 eV, and two smaller unidentified peaks of the form TiN_xO_y at 398.5 and 401.3 eV, respectively.

In UHMWPE, ion ionization interactions lead to the cross-linking of the surface layer producing surfaces with greater hardness (27, 28). As expected in this study, the implanted samples exhibited an increase in hardness, and an increase of more than twofold was observed in the Ti6Al4V alloy and fourfold in the UHMWPE at a load of 1 gf (Tab. I).

It was seen that the surface color of the modified

UHMWPE wear pins had changed from white to dark brown, believed to be caused by processes involving thermal effect and dehydrogenation (29). During implantation, highly energetic N⁺ ions pass through the UHMWPE surface, and some of their energy dissipates onto the treated surface as heat. No change in color was observed on the Ti6Al4V samples. AFM images of modified and unmodified samples are shown in Figures 5 (a, and b) and 6 (a, and b), respectively, for Ti6Al4V and UHMWPE prior to any test. As shown, the image revealed some regular blistering patterns on the modified Ti6Al4V (Fig. 5b), believed to be due to ion beam bombardment of the energetic ions. During implantation, two N⁺ ions can also react together to form N₂ gas bubbles on the material surface (30). The modified UHMWPE surfaces (Fig. 6b) looked featureless except for occasional microtoming scratch marks.

Wear test results expressed in mean volume loss of the UHMWPE wear pins against sliding distance are shown in Figure 7, and Table II shows the mean UHMWPE wear factors (k_o) calculated for each test, and the weight loss of Ti6Al4V after testing. It is apparent by comparison with Figure 7 (error bars within symbols) that the wear of N⁺ ion-implanted UHMWPE wear pins was significantly reduced when tested against N⁺ ion-implanted Ti6Al4V plates. Table III shows the R_a values of the materials before and after wear tests. N⁺ ion implantation had no effect on the R_a of the materials.

During UHMWPE/Ti6Al4V and N⁺ ion-implanted

TABLE II - MEAN UHMWPE k_o AND Ti6Al4V WEIGHT LOSS AFTER 5.5 MILLION CYCLES

Material couple tested	UHMWPE $k_o \times 10^{-6}$ (mm ³ /Nm)	Ti6Al4V weight loss (μg)
UHMWPE Ti6Al4V	2.77 ± 0.16	214 ± 0.08
N ⁺ ion-implanted UHMWPE Ti6Al4V	2.42 ± 0.07	198 ± 0.08
UHMWPE N ⁺ ion-implanted Ti6Al4V	1.65 ± 0.05	81 ± 0.06
N ⁺ ion-implanted UHMWPE N ⁺ ion-implanted Ti6Al4V	1.25 ± 0.05	79 ± 0.0

TABLE III - MATERIAL ARITHMETIC MEAN SURFACE ROUGHNESS (R_a)

Material surface	R_a (μm)	
	Pre-test	Post-test
Ti6Al4V	0.008	0.08
N ⁺ ion-implanted Ti6Al4V	0.009	0.02
UHMWPE	1.2	0.005
N ⁺ ion-implanted UHMWPE	1.3	0.005

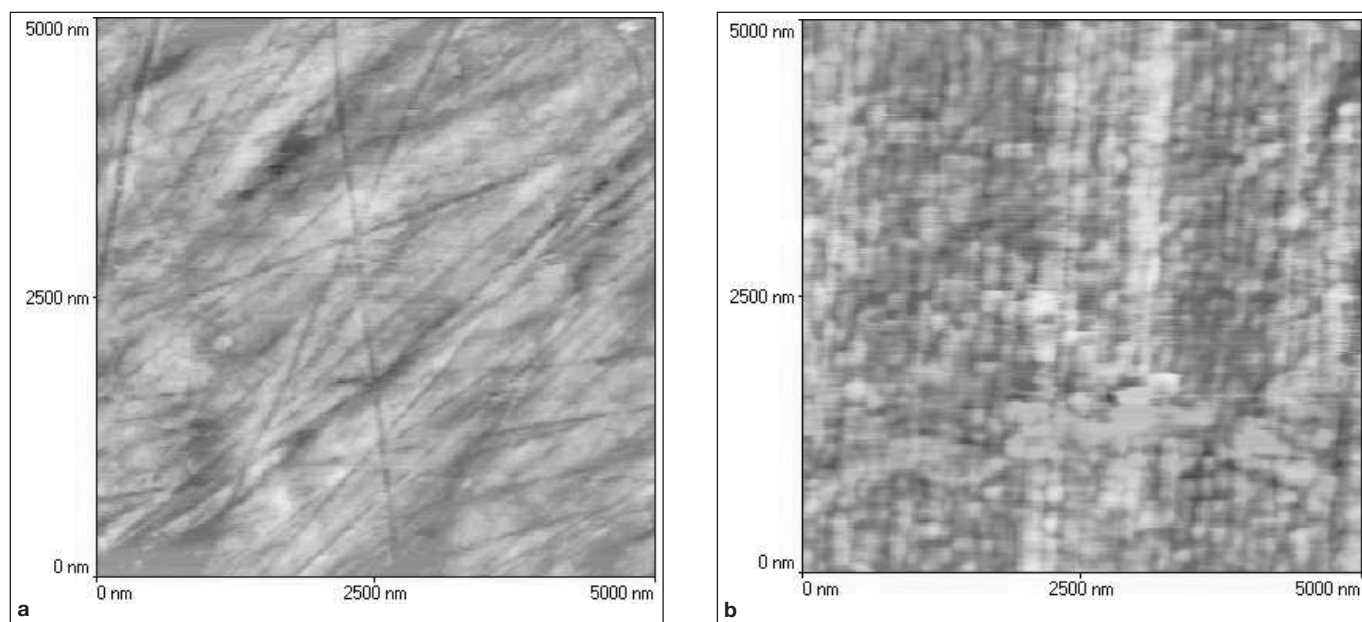


Fig. 5 - AFM images of Ti6Al4V (pre-wear test), a) unmodified and b) N⁺ ion-implanted.

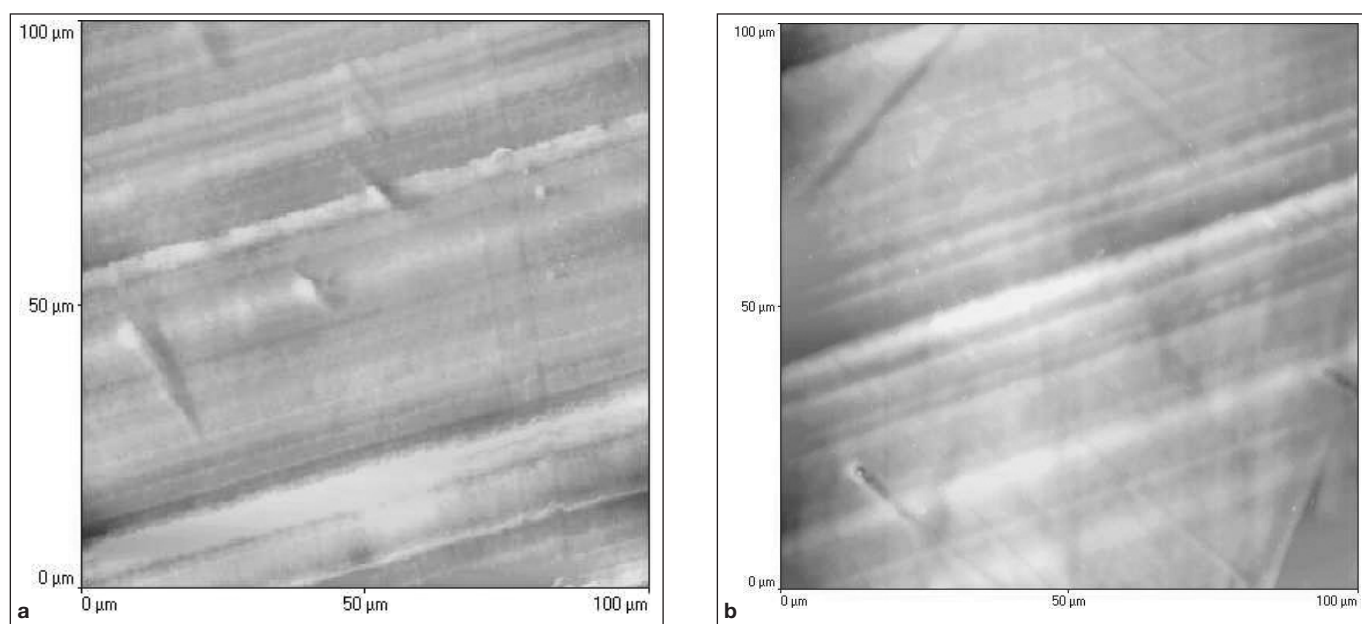


Fig. 6 - AFM images of UHMWPE (pre-wear test), a) unmodified and b) N⁺ ion-implanted.

UHMWPE/Ti6Al4V sliding couple tests, severe damage was visible on the Ti6Al4V plates in the wear tracks after a few cycles and increased with test duration. The bovine serum lubricant turned black with test duration and contained dark debris, found to be titanium oxide particles (6, 9). Wear pins showed embedded black debris on their worn area, because of the oxide particles transferred from the worn plates. The continuous rotation and reciprocation

action of the UHMWPE pins broke the surface passive oxide layer on the Ti6Al4V plates during testing, and this hard debris remained between the pin and the plate. The debris starts a severe abrasive process, resulting in a quick deterioration of both Ti6Al4V and UHMWPE. The oxide layer reforms rapidly after removal and increases the abrasion mechanism (31). It is well known that there is a strong adhesion between UHMWPE and the tita-

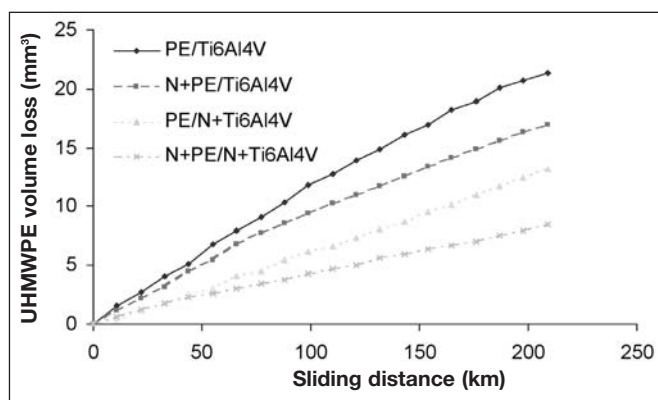


Fig. 7 - Wear behavior of Ti6Al4V/ UHMWPE sliding couples.

nium oxide film, and this promotes the three-body abrasive wear (31-33). This explains the high wear factors obtained for UHMWPE sliding against unmodified Ti6Al4V. AFM (Fig. 8) and non-contacting interferometry revealed distinctive wear tracks characterized by random severe scratches and grooves in the wear tracks of the Ti6Al4V plates, and higher R_a values (Tab. III), an indication of severe abrasive wear.

On the other hand, testing with UHMWPE/ N^+ ion-implanted Ti6Al4V, and N^+ ion-implanted UHMWPE/ N^+ ion-implanted Ti6Al4V couples showed little or no damage in the wear tracks of the Ti6Al4V plates (Fig. 9), and no black debris were observed in the lubricant over the duration of the test. It is known that N^+ ion implantation can retard the start of severe abrasive wear in Ti6Al4V alloys; however, the precise mechanism that delays the onset of abrasive wear is not yet clear (25, 32). The TiN precipitate that forms on the Ti6Al4V surface stabilizes the protective outer oxide layer and leads to a reduction of oxide particles removed from the surface; and therefore, a reduction in the wear of the mating UHMWPE. XPS energy spectrum of the wear track region of the implanted Ti6Al4V post-wear tests (Fig. 10), had the same binding energy positions as seen on the pre-wear tested material (Fig. 3), an indication of TiN presence. However, high-resolution XPS analysis of the Ti 2p was clearly depleted in TiN relative to TiO_2 , when compared to that from the pre-wear material, indicating TiN depletion with test duration.

To date, N^+ ion implantation has been successfully applied in metallic and polymeric biomaterials. In metal alloys, physical changes induced by the process are due to atomic and nuclear collisions, which often lead to the formation of highly disordered structures in the near-surface region. Chem-

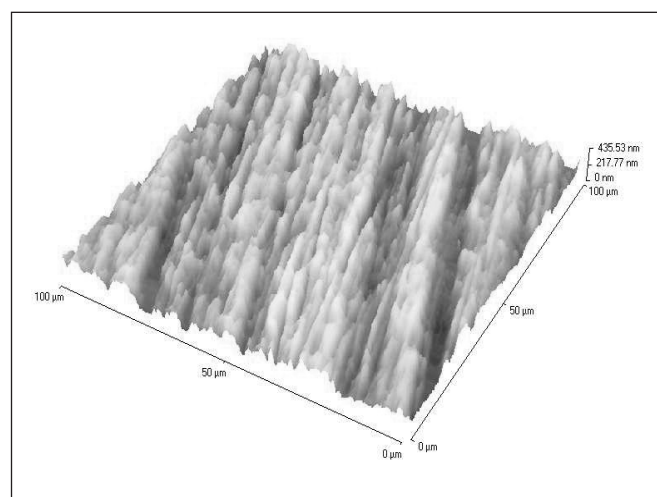


Fig. 8 - AFM image of worn Ti6Al4V surface (post-wear).

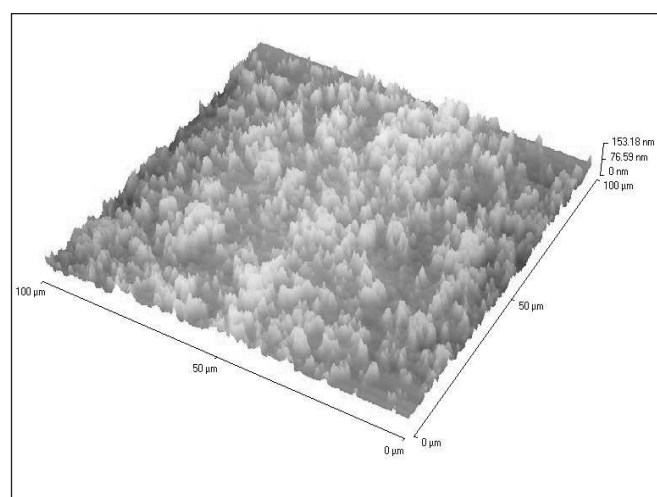


Fig. 9 - AFM image of worn N^+ ion-implanted Ti6Al4V surface (post-wear).

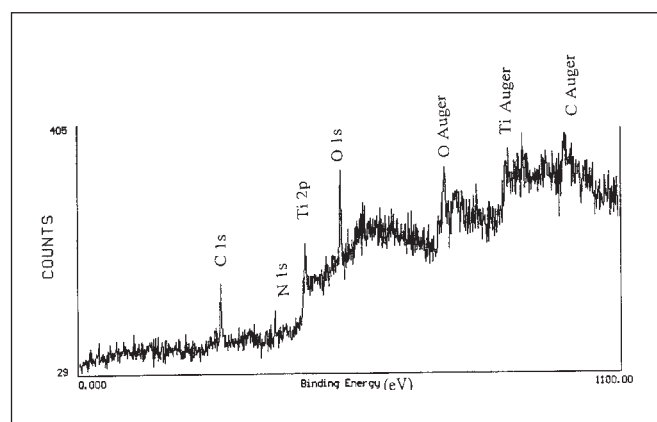


Fig. 10 - XPS energy spectrum of worn ion-implanted Ti6Al4V.

ical changes arise from the formation of hard-phase nitride precipitates because of chemical bond formations between the substrate atoms and implanted active N⁺ ion species. The physical and chemical changes typically combine to create surfaces that are harder, and more resistant to wear and chemical attack, without changing any of the metal bulk properties (1-3). As expected in this study, increases in surface hardness, low removal of oxide particles and hence low wear, were observed on the N⁺ ion-implanted Ti6Al4V.

In polymer biomaterials, numerous effects are observed because of N⁺ ion implantation. The entire implantation process can be understood as the end result of two major competing processes: cross-linking and chain scission (1, 3, 27). An ion penetrating a polymer surface interacts with substrate atoms primarily through ionization, and recoil interactions. Ionization is dominant, and generally leads to cross-linking in adjacent polymer chains, whereas recoils generally lead to chain scission. The cross-linking process creates a three-dimensionally cross-linked surface layer with greater hardness and improved wear resistance, as observed in this study. Implantation sometimes results in selective enhancement or reduction of functional chemical groups, which can, by modifying chemical interactions on the polymer surface, effect changes in surface wettability.

In many ways, the effects observed as a result of ion implantation in polymers, are similar to those produced by treatment with common ionizing radiation (3), where some stability problems such as oxidation and degradation due to chain breakage and, perhaps, free radical interactions with O also occur (34). However, irradiation treatments are always followed by thermal stabilization processes (35), and studies have shown that (36-38) it is necessary to perform a stabilization treatment to enhance cross-linking and to reduce the possibility of polymer degradation by oxidation and extraction of radicals. Such a stabilization treatment also increases the likelihood of eliminating free radicals; therefore, preventing their reaction with diffused O during storage (in the absence of vacuum packaging) and improving cross-linking during *in vivo* service (34, 35). The ion implantation conditions used in this study promoted cross-linking effects (high energies >10 KeV), and reduced oxidation effects (high vacuum environment). However, if such stability problems were present in this study, the outcome of the modified Ti6Al4V/modified UHMWPE sliding couple wear, in particular, could change in the long term. Therefore, stabilization treatments followed by sterilization should be carried out following ion implantation in further studies, to

enhance cross-linking, and to prevent the reformation of free radicals during long-term use.

CONCLUSIONS

Three-body abrasive wear dominated unmodified Ti6Al4V/UHMWPE sliding couple tribology, leading to extensive surface damage of the alloy and high wear of the mating UHMWPE. These conclusions were consistent with clinical observations.

N⁺ ion implantation improved the surface hardness and the wear of Ti6Al4V and, in turn, improved the wear of the mating UHMWPE. The enhanced tribological properties of the alloy impeded third body formation and reduced UHMWPE wear. Tests with all implanted couples showed the most improved tribological performance.

The results demonstrated a definite potential for the use of N⁺ ion-implanted Ti6Al4V as the bearing surface in TJR applications. However, since only one energy-dose combination was investigated, it is not yet clear what implantation parameters lead to an optimized tribological behavior. Therefore, additional work using a range of ion energies and doses is necessary to develop an optimum N⁺ ion implantation surface modification protocol.

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